Phosphorylation

(from prior exam 1 notes)

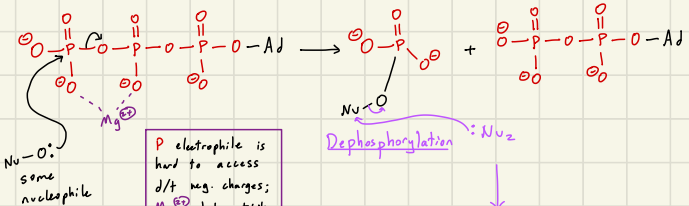
Phosphate Bonds

Thermodynamically favorable $\Delta G << 0$

Kinetically unfavorable d/t neg charges

(needs Mg^{2+} to lower E_a)

→ can also stabilize other ⊖ eg $\overset{\ominus}{O}$ in other enzymes



Names

ATP = ad- 3 phosphates

ADP = ad- 2 phosphates

AMP = ad- 1 phosphate

P_i = free PO_4^{3-}

PP_i = free $PO_3^{2-}-PO_3^{2-}$

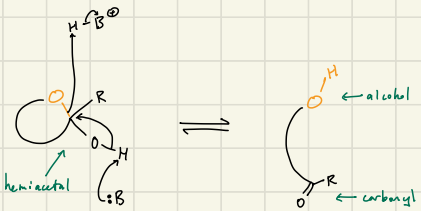
Enzyme Names!

- Kinase
- Phosphorylase (add P_i)
- Phosphatase (remove P_i)

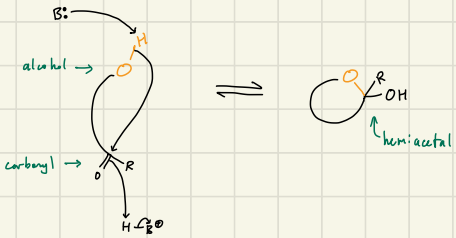
Ring break/form (aka hemiacetal formation = connect/disconnect C–O bond)

(Chem 17 review)

ring break:

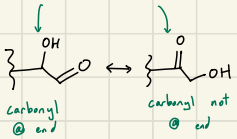


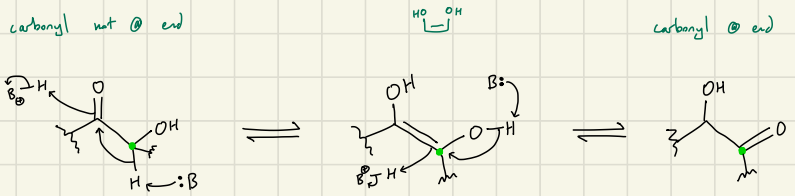
ring form:



No specific enzyme names

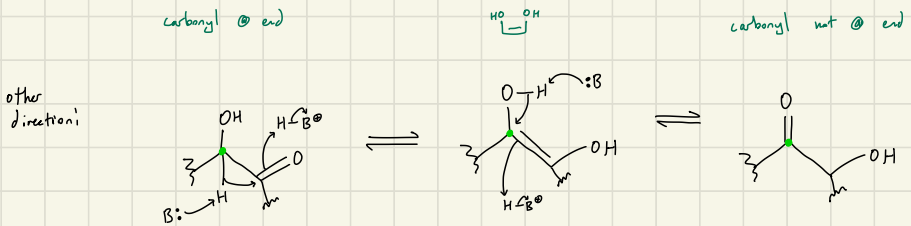
Aldose - Ketose Isomerization

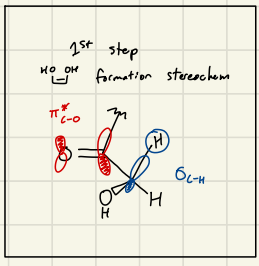


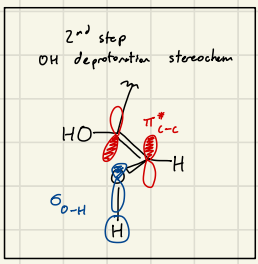


① OH's carbon deprotonated → double bond, carbonyl → another new OH

② old OH → new carbonyl, double bond reprotonated → single bond







Enzymes:

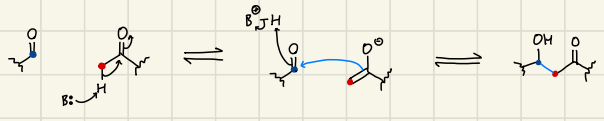
Isomerase

Aldol / Retro-Aldol = connect / disconnect C–C bond

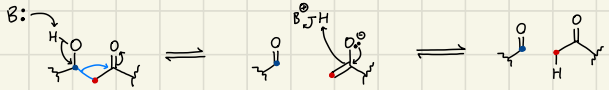
form C–C! (aldol)

① form enolate

② enolate nucleophile → make C–C bond



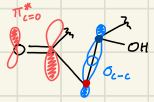
break C–C! (retroaldol)



① unmake C–C bond

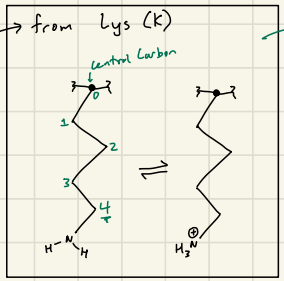
② unform enolate

stereochem for break C–C



Aldol / Retro-Aldol w Imine

from Lys (K)



Why w imine?

OH = not (good nuc)

form C–C!

avoid neg charge O⁻ = enol

use enamine N = nuc instead

break C–C!

imine N⊕ better electroph. than O

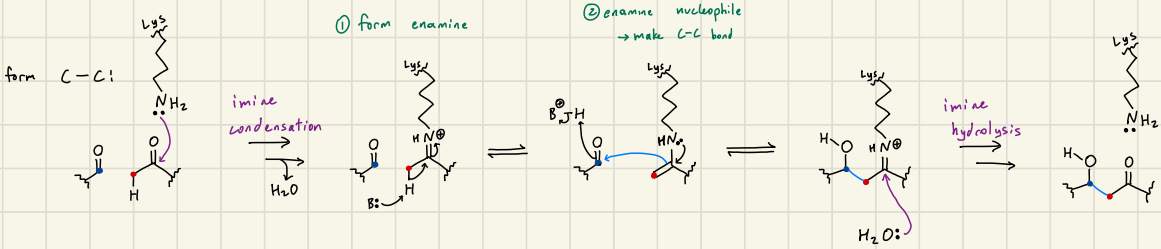
form C–C!

① form enamine

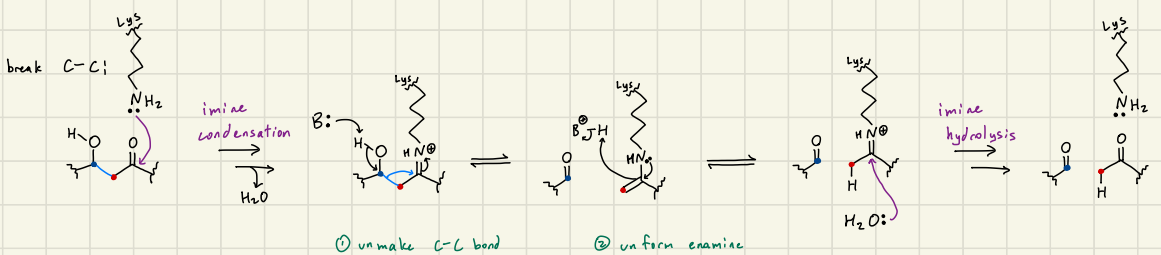
② enamine nucleophile → make C–C bond

imine condensation

imine hydrolysis



break C–C!



① unmake C–C bond

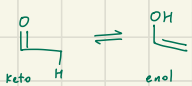
② unform enamine

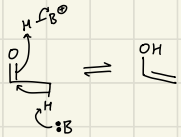
Enzymes!

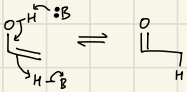
Aldolase

Keto-enol Tautomerization

from chem 17







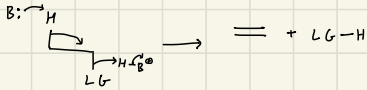
no specific enzymes

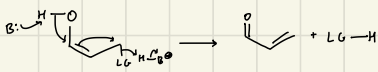
E1cb mechanism

eliminate something using extra e⊖ for double bond formation

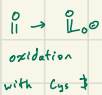
from Chem 17

Examples:



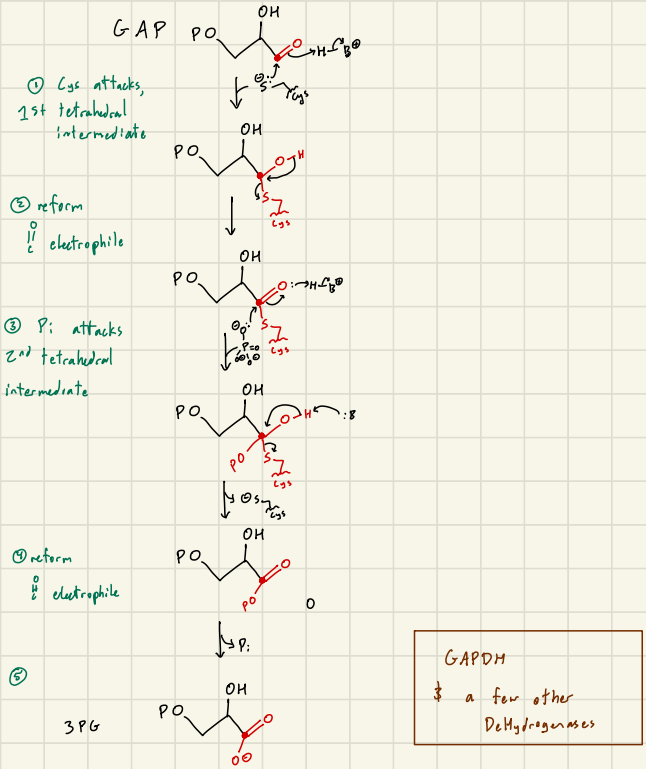


GAPDH



oxidation

with Cys & P_i



GAPDH

& a few other DeHydrogenases

Decarboxylation

Chem 17

CO_2 leaves via pushing old C–C bond $e^{\ominus}$ onto good $e^{\ominus}$ sink! eg ⊕ charge,

resonance,

good electrophiles

ex.